

# CERTIFICATION OF TRANSLATION

I, <u>Yong-woon Kim</u>, an employee of Y.P. LEE, MOCK & PARTNERS of The Cheonghwa Bldg., 1571-18 Seocho-dong, Seocho-gu, Seoul, Republic of Korea, hereby declare under penalty of perjury that I understand the Korean language and the English language; that I am fully capable of translating from Korean to English and vice versa; and that, to the best of my knowledge and belief, the statement in the English language in the attached translation of <u>Korean Patent Application No. 10-2002-0044502</u> consisting of 35 pages, have the same meanings as the statements in the Korean language in the original document, a copy of which I have examined.

Signed this 21th day of April 2005

yongwoon kim



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#### SINGLE LAYERED ELECTROPHOTOGRAPHIC PHOTORECEPTOR

### **BACKGROUND OF INVENTION**

### 5 1. Field of Invention

The present invention relates to a single layered electrophotographic photoreceptor, more particularly, to a single layered electrophotographic photoreceptor, which makes it possible to obtain better image by suppressing a decrease in dark decay and electric potential due to repeated use, and its electrical lifetime is extended.

### 2. Description of Related Art

Electrophotographic method refers to a method comprising; exposing a surface of a photoconductive cell selectively to form a latent image; making a difference in electrostatic charge density between the exposed area and the unexposed area; and forming a visible image using electrostatic toner including a pigment or a thermoplastic component.

In the electrophotographic method, so called wet developing method using a liquid developer is well known in the art as described in US 2,907,674, US 3,337,340, etc. and it has an advantage of obtaining a high resolution image, since diameters of toner particles can be reduced to sub-microns.

But, the wet developing method has a problem in that its major component, petroleum solvent, has an odor and is easily ignited. So a dry developing method, which uses power developer, is more commonly used nowadays.

Despite of the problems mentioned above, needs to use the wet developing method are increasing because of its advantage of high resolution.

The wet developing method refers to a method comprising; forming an electrostatic image on a surface of the photoreceptor, and sometimes moving the electrostatic image to another surface; and wetting the surface with a liquid carrier,

which has an electrostatic resistance enough to suppress a destruction of the electrostatic image and has a pigment.

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Meanwhile, in the wet developing method, inorganic photoreceptor such as amorphous selenium has been widely used as an electrophotographic photoreceptor. But, recently, organic photoreceptor is used, and following problems have arisen.

If the surface of the organic photoreceptor is consisted of a binder such as polycarbonate resin and acrylic resin, and a charge transport layer including a low molecular compound charge transport material, the charge transport layer forming materials have a solubility to an aliphatic carbohydrate solvent of the liquid developer, and the liquid developer may be prepared by dispersing stain particles in the aliphatic carbohydrate solvent.

Therefore, when the liquid developer is in direct contact with the organic photoreceptor, a crack or a decrease of an exposure to a light happens due to an erosion of photoreceptor by the solvent, or eluted photoreceptor contaminates the developer.

To solve the problems mentioned above, many researches have been made to develop a photoreceptor, which has an improved endurance to a liquid developer, and there are following 3 representative methods.

- (1) Polymerizing components of the photoreceptor, for example charge transport material, to prevent elution.
- (2) Preparing a surface protection layer, which has an increased endurance against developer, to prevent the solvent from invading the layer of the photoreceptor.
- (3) Improving the endurance of the binder against the developer, to prevent the solvent from invading the layer of the photoreceptor.

A prior art related to the method (1) is disclosed in US 5,030,532. But, according to the disclosure above mentioned, there are limited number of highly

solvent-resistant polymeric charge transport materials, and conventional resins may not be used, so that the production cost is very high.

Another prior art related to the method (2) is disclosed in US 5,368,967. But, according to the disclosure above mentioned, the manufacturing process is too complicated, and the surface protection layer should be thin not to affect the characteristics of the photoreceptor, hence the endurance is deteriorated.

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Still another prior art related to the method (3) is disclosed in US 5,545,499. According to this disclosure, it is difficult to ensure the endurance of the photoreceptor against the solvent by the binder alone, and there hasn't been any practical one.

Furthermore, JP Laid-Open Pub. No. Hei. 5-297601, JP Laid-Open Pub. No. Hei. 7-281456, and JP Laid-Open Pub. No. Hei. 10-20515 disclose organic photoreceptor using polyester resin as a binder, which has a main chain composed of biphenyl fluorene repeating units, but these patents are based on a general electrophotographic method, and are intended to improve mechanical endurance using specific polyester resins, and have no descriptions whether they can be applied to a wet developing method. Also, since the resins disclosed in the above patents have poor electrical characteristics, they have not been in practical use.

Generally, electrophotographic receptor is prepared by forming a photoreceptor layer composed of charge generating material, charge transporting material and binder resins etc. on a conductive substrate. As a photoreceptor layer, a function-separated layer-built photoreceptor layer, which is prepared by laminating a charge generating layer and a charge transporting layer, is commonly used. And also, a single layered photoreceptor layer which can be prepared by a simple manufacturing procedure attracts attentions because of an advantage of positively charged characteristics, which make it possible to be used in low ozone generating positive corona discharge, and a lot of researches have been made on it.

As a single layered photoreceptor layer, for example, a photoreceptor layer composed of PVK/TNF charge movable complex disclosed in US3,484,237, a

photoreceptor layer composed of photoconductive phthalocyanine layer dispersed on a resin disclosed in US3,397,086, and a photoreceptor layer composed of coagulant of thiapyrylium and polycarbonate dispersed on a resin with a charge transporting material disclosed in US3,615,414 are representative ones, but these photoreceptor layers are not currently used because of insufficient electrostatic characteristics, a limitation in the choice of materials, and toxicity.

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The most commonly used single layered photoreceptor layer is the one which is comprised of charge generating materials together with hole transporting materials and electron transporting materials, are dispersed on resins, and it is disclosed in JP Laid-Open Pub. No. Sho. 54-1633. It is advantageous in that variety of materials may be chosen since the generation and the transportation of the charge are functionally separated in each material, and that functional and chemical endurance of the photoreceptor layer may be improved since a low concentration of the charge generating materials can be used.

The photoreceptor may perform basic performances of forming images by adopting the single layered photoreceptor layer only, but in practical, it is important to obtain better images and to maintain those images for a long time without any loss of image in case of repeated and long time use is required.

But, corona discharge to charge the photoreceptor produces a lot of ozone, and this reactive ozone reacts with nitrogen or oxygen in the atmosphere to form ozone or nitrogen oxide (NOx). The resulting ozone or nitrogen oxide is highly reactive that it may change the properties of the surface of the photoreceptor, and make it difficult to obtain good images without defects. Even more OPC drum with this kind of photoreceptor has a short electrical lifetime when it is used for a long period of time.

#### SUMMARY OF THE INVENTION

Therefore, the present invention provides an electrophotographic photoreceptor, which is highly resistant to liquid developer used in wet developing

method, produces good images since the change in the properties of the surface of the photoreceptor is suppressed, and whose electrical lifetime is extended.

Further, the present invention provides an electrophotographic device with the electrophotographic photoreceptor.

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### **DETAILED DESCRIPTION OF THE INVENTION**

According to the first embodiment of the present invention, the present invention provides an electrophotographic photoreceptor comprises:

a conductive substrate; and

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a photoreceptor layer formed on the substrate comprising polyester resins which have biphenyl fluorene units of following general formula (1) in the main chain as binding resins, and phenolic compounds which have following general formula (2) as antioxidants:

Formula (1)

Formula (2)

$$X_{1} = X_{2}$$

$$X_{1} = X_{2}$$

$$X_{2}$$

wherein, in the formula (1), the hydrogens in the aromatic rings may or may not be substituted with substituents selected from a group consisting of halogen,  $C_{1}$ - $C_{20}$  aliphatic hydrocarbon, and  $C_{5}$ - $C_{8}$  cycloalkyl;

wherein, in the formula (2),  $X_1$  and  $X_2$ , independently each other, are hydrogen or  $C_1$ - $C_6$  alkyl,  $Y_1$  and  $Y_2$ , independently each other, are hydrogen, methyl or ethyl, and  $X_3$  is selected from a group consisting of following  $C_1$ - $C_6$  alkyls;

$$-(CH_2)_{\overline{a}}(COO)_{\overline{b}}(CH_2)_{\overline{c}} \xrightarrow{Y_1} X_1$$

$$X_1$$

$$X_1$$

$$X_2$$

$$Y_2$$

or 
$$\begin{array}{c|c} X_1 & X_1 & X_1 \\ X_1 & X_2 & X_3 & X_4 & X_2 \end{array}$$

wherein, in  $X_3$ , a, c, k, I, and m is an integer of 0 to 6, b is 0 or 1,  $X_1$  and  $X_2$ , independently each other, are hydrogen or  $C_1$ - $C_6$  alkyl,  $Y_1$  and  $Y_2$ , independently each other, are hydrogen, methyl or ethyl, and  $X_4$ ,  $X_5$ , and  $X_6$ , independently each other, are hydrogen or  $C_1$ - $C_6$  alkyl.

According to the second embodiment of the present invention, the present invention provides an electrophotographic photoreceptor comprises:

a conductive substrate; and

a photoreceptor layer formed on the substrate comprising polyester resins which have biphenyl fluorene units of following general formula (1) in the main chain as binding resins, and phenolic compounds which have following general formula (3) as antioxidants:

Formula (1)

### Formula (3)

$$\begin{bmatrix} X_1 & & & \\ & X_1 & & & \\ & & & \\ &$$

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wherein, in the formula (1), the hydrogens in the aromatic rings may or may not be substituted with substituents selected from a group consisting of halogen,  $C_{1}$ - $C_{20}$  aliphatic hydrocarbon, and  $C_{5}$ - $C_{8}$  cycloalkyl;

wherein, in the formula (3),  $X_1$  and  $X_2$ , independently each other, are hydrogen or  $C_1$ - $C_6$  alkyl, a and c is an integer of 0 to 6, b is an integer of 0 or 1, n is an integer of 2 to 4, Z is S or O when n is 2, N when n is 3, and C when n is 3.

In the electrophotographic photoreceptor according to the first and the second embodiments of the present invention, the polyester resin may be a polyester resin comprising repeating units of following general formula (4), (5) or (6), or a copolymer comprising more than two of the repeating units.

### Formula (4)

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### Formula (5)

### Formula (6)

In the electrophotographic photoreceptor according to the first and the second embodiments of the present invention, preferably, the polyester resin may be a compound of a following general formula (7) or (8).

### Formula (7)

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Wherein, m and n, independently each other, are an integer of 10 to 1,000. Formula (8)

Wherein, k is an integer of 10 to 1,000.

In the electrophotographic photoreceptor according to the first and the second embodiments of the present invention, preferably, the content of the antioxidant may be from 0.01wt% to 50wt% of the total weight of the charge transporting material of the photoreceptor layer.

In the the electrophotographic photoreceptor according to the first embodiment of the present invention, preferably, the antioxidant of the general formula (2) is a compound selected from a group consisting of compounds of general formula (9), (10), (11) and (12).

## Formula (9)

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## Formula (10)

### Formula (11)

## Formula (12)

In the electrophotographic photoreceptor according to the second embodiment of the present invention, preferably, the antioxidant of the general formula (3) is a compound of general formula (13) or (14).

# Formula (13)

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## Formula (14)

In the electrophotographic photoreceptor according to the first and the second embodiments of the present invention, preferably, the electrophotographic photoreceptor is a electrophotographic photoreceptor for a wet developing method.

Further, the present invention provides an electrophotographic device with the electrophotographic photoreceptor according to the first and the second embodiments of the present invention.

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The electrophotographic photoreceptor according to the present invention is highly resistant to liquid developer by using polyester resins with a specific structure as binding resins, produces good images even though it has single photoreceptor layer since a decrease in electrical potential of photoreceptor due to corona discharge is suppressed by using antioxidants with a specific structure, and has extended electrical lifetime.

It is assumed that a mechanism through which the electrophotographic photoreceptor according to the present invention with the antioxidants having the specific structure can produce good images and can have extended lifetime is as follows.

The antioxidants according to the present invention having the specific structure can prevent oxidants produced during charging or exposing to a light such as ozone or nitric oxide etc. from oxidizing the photoreceptor, which comprises binding resins, electron transporting materials and hole transporting materials. Therefore, the electrophotographic photoreceptor according to the present invention can produce good images even though it is used repeatedly since it can suppress the decrease in the electrical potential and the dark decay, and as a result, its electrical lifetime can be extended. Also, even though the electrophotographic photoreceptor according to the present invention is an organic photoreceptor, it can be applied to the wet developing method suitably, since its endurance against the liquid developer is good with the aid of binding resins, which are polyester resins having the specific structures.

The electrophotographic photoreceptor according to the present invention is the single layered photoreceptor comprising both a charge generating material and an electron transporting material in the photoreceptor layer sprayed on a conductive substrate. As a conductive substrate, a drum or a belt made of metal or plastic can be used.

As mentioned above, the photoreceptor layer comprises the charge generating materials, the hole transporting materials and the electron transpoting materials.

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As a charge generating material, for example, organic materials such as phthalocyanine pigments, azo pigments, quinone pigments, perylene pigments, indigo pigments, bisbenzoimidazole pigments, quinacridone pigments, azulenium pigments, squarylium pigments, pyrylium pigments, triarylmethane pigments, cyanine piments, and inorganic materials such as amorphous silicon, amorphous selen, trigonal selen, tellurium, selen-tellurium alloy, cadmium sulfide, antimony sulfide, zinc sulfide can be used. Available charge generating materials are not limited to the listed compounds herein, and these compounds can be used alone or in combination with other charge generating materials.

The ratio of the charge generating materials in the photoreceptor layer is, preferably, from 2wt% to 10wt%. If the ratio is too small, light absorption of the photoreceptor is poor, and sensitivity is decreased due to a large energy loss. If the ratio is too large, charge characteristic is poor due to an increased dark conduction, and sensitivity is decreased due to a decreased mobility caused by an increased trap density.

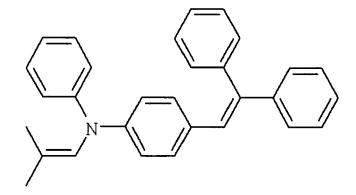
As a hole transporting material of the electrophotographic photoreceptor according to the present invention, for example, nitrogen containing cyclic compounds or condensed multi-cyclic compounds of pyrenes, carbazoles, hydrazines, oxazoles, oxadiazoles, pyrazolines, arylamines, arylmethanes, benzidines, thiazoles, styryls, or mixture of these compounds can be used. Also,

polymers or polysilanes having the above substituents in the main chain or side chains can be used.

The hole transporting materials, preferably, have a structure selected from following listed structures.

## Formula (15)

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## Formula (16)

# Formula (17)

# Formula (18)

# Formula (19)

# Formula (20)

### Formula (21)

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The hole transporting materials are disclosed in US5,013,623, and can be easily synthesized from the disclosure.

As an electron transporting material of the electrophotographic photoreceptor according to the present invention, for example, electron receiving materials such as benzoquinones, cyanoethylenes, cyanoquinodimethanes, fluorenes, xanthones, phenantraquinones, anhydrous phthalic acids, thiopyranes, diphenoquinones, or mixture of these compounds can be used. But, available electron transporting materials are not limited to the listed compounds herein, therefore electron transporting polymers and pigments having the above substituents in the main chain or side chains can be used.

The electron transporting materials, preferably, have a structure selected from following listed structures.

# Formula (22)

# Formula (23)

# 5 Formula (24)

The electron transporting materials are disclosed in US4,474,865, and can be easily synthesized from the disclosure.

The weight ratio of the hole transporting materials to the electron transporting materials is, preferably, from 9:1 to 1:1. If the ratio is not in the above range, mobility of the holes and the electrons to exert a substantial performance as a photoreceptor cannot be obtained.

The percentage of the charge transporting materials, that is the sum of the hole transporting materials and the electron transporting materials, in the photoreceptor layer is, preferably, from 10wt% to 60wt%. If it is below 10wt%, the charge transporting capacity is not sufficient to obtain good sensitivity, and a residual potential grows bigger. If it is above 60wt%, the layer is not strong enough, since the amount of the resins contained in the photoreceptor layer is too small.

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The photoreceptor layer according to present invention includes polyester resins having biphenylfluorene unit represented in formula (1) in the main chain as binding resins. These binding resins are highly resistant to aliphatic carbohydrate solvent that they make the electrophotographic photoreceptor of the present invention especially acceptable to electrophotographic devices using the wet developing method. Preferably, among the polyester resins represented in formula (1), the polyester resins which have repeating units represented in formula (4), (5), and (6) or the copolymers which have more than two of these repeating units can be used, and polyester resins represented in formula (7) and (8) are especially preferable.

The polyester resins, which have biphenylfluorene unit represented in formula (1) in the main chain, can be used in combination with other conventional binding resins as well as can be used by themselves. The conventional binding resins include, for example, polycarbonate resins such as bisphenol-A type polycarbonate (Teijin Chemical Co., Ltd., 'PANLITE'), and bisphenol-Z type polycarbonate (Mitsubishi Gas Chemical Co., Ltd., 'IUPILON Z-200'), metaacrylic resins (Mitsubishi Rayon Co., Ltd., 'DIANAL'), conventional polyester resins (Japan Toyo Spinning Co., Ltd., 'Vylon-200'), and polystyrene resins (Dow Chemical Co., Ltd., 'STYLON').

The weight percentage of the polyester resins having biphenylfluorene unit represented in formula (1) is, preferably from 50wt% to 100wt% of the total weight of the binder used in the photoreceptor. If the weight percentage of the polyester resins having biphenylfluorene unit represented in formula (1) is below 50wt% of the total weight of the binder, the endurance to liquid developer may be poor.

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The photoreceptor according to the present invention includes phenolic antioxidants having the specific structure, and the phenolic compounds represented in formula (2) and (3) can be, preferably used. The examples of the antioxidants represented in formula (1) are the phenolic compounds represented in formula (9), (10), (11) and (12), and the examples of the antioxidants represented in formula (3) are the compounds represented in formula (13) and (14), but not limited thereto.

The weight percentage of the antioxidants is, preferably from 0.01wt% to 50wt% of the total weight of the charge transporting materials of the photoreceptor layer. If the weight percentage of the antioxidants is below 0.01wt% of the total weight of the charge transporting materials, the stability of the electrical potential is poor, and if it is above 50wt%, the increase in the exposure potential is too big.

The phenolic antioxidants can be used in combination as well as can be used alone. Also, they can be used in combination with other antioxidants, for example, sulfuric antioxidants, phosphorous antioxidants, and amine antioxidants.

The present invention provides the method of preparing the electophotographic photoreceptor according to the present invention.

The electrophotographic photoreceptor is prepared by coating and drying the charge generating materials, the charge transporting materials, the binding resins and the photoreceptor layer forming materials including solvent on the conductive substrate. The binding resins should comprise the polyester resins having biphenylfluorene repeating units represented in formula (1) in the main chain of the polyester. Preferably, the weight percentage of the binding resins is, from 40wt% to 90wt% of the total solid weight of the composition for forming the photoreceptor layer, and the weight percentage of the polyester resins having biphenylfluorene

repeating units represented in formula (1) in the main chain of the polyester is, from 50wt% to 100wt% of the total weight of the binder included in the composition for forming the photoreceptor layer.

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The solvent used in the composition for forming the photoreceptor layer, for example, is selected from organic solvents such as alcohols, ketones, amides, ethers, esters, sulfones, aromatics, and aliphatic halogenated carbohydrates. The examples of alcohols include methanol, ethanol, butanol, and isopropylalcohol, examples of ketones include acetone, methylethyl ketone, and cyclohexanone, the examples of amides include N,N-dimethyl formamide, and N,N-dimethyl acetoamide, the examples of esters include ethyl acetate, and methyl acetate, the examples of sulfones include dimethyl sulfoxide and sulforan, the examples of aromatics include benzene, toluene, xylene, monochlorobenzene, and dichlorobenzene, and the examples of aliphatic halogenated carbohydrates include methylene chloride, chloroform, tetrachlorocarbon, and trichloroethane. The content of the solvents is, preferably, from 2 to 100 parts by weight based on 1 part by weight of the solid composition for forming the photoreceptor layer.

Methods for coating the composition for forming the photoreceptor layer include, for example, ring coating, dip coating, roll coating, and spray coating, but not limited thereto. The thickness of photoreceptor layer according to the methods is, preferably, from  $5\mu m$  to  $50\mu m$ .

It is also possible to place an intermediate layer between the conductive substrate and the photoreceptor layer to increase adhesiveness, and to prevent charge influx from the substrate. The examples of the intermediate layer include, for example, cathod oxidation layer of AI; resin dispersion layer of metal oxide particles such as titanium oxide, tin dioxide; resin layer of polyvinyl alcohol, casein, ethyl cellulose, gelatin, phenol resin, polyamide, but not limited thereto.

Also, additives such as plasticizer, leveling agent, dispersion stabilizer, and photostabilizer together with the binding resins can be added in the photoreceptor

layer of the present invention. Examples of the photostabilizer include benzotriazole compounds, benzophenone compounds, and hindered amine compounds.

The invention is further described by the following examples. The examples are only for the purposes of illustration. It should be understood that the invention is not limited to the specific details of the examples.

### Example 1

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8 parts by weight of  $\gamma$ -type titanyloxy phthalocyanine ( $\gamma$ -TiOPc) as the charge generating materials, 35 parts by weight of the compound represented in formula (15) as the hole transporting materials, 15 parts by weight of butyl-9-dicyanomethylenefluorene-4-carboxylate(BCMF) represented in formula (22) as the electron transporting materials, 60 parts by weight of polyester resins represented in formula (7) (Kanebo Co., Ltd., O-PET, m/n=7/3, Mw=40,000) as the binding resins, and 5 parts by weight of phenolic compounds represented in formula (13) as the antioxidants, are mixed in cosolvent, of which weight ratio of 1,1,2-trichloroethane/methylene dichloride is 4/6, to be 23wt% concentration, and the composition for forming the photoreceptor layer is obtained by abrasive milling for 2 hours in 5  $^{\circ}$ C using milling machine (Dispermat Co., Ltd.). The average diameter of the  $\gamma$ -TiOPc particles dispersed in the composition was about 0.3 $\mu$ m.

The composition was sprayed on a Al drum, which has a diameter of 30mm, using ring coating method, and then dried for an hour in 110  $^{\circ}$ C to obtain single layered electrophotographic photoreceptor of 20 $\mu$ m thickness.

### Example 2

Except that 10 parts by weight of the phenolic compound represented in formula (13) were used as antioxidants, single layered electrophotographic photoreceptor of 20µm thickness was obtained by the same method as Example 1.

### Example 3

Except that 5 parts by weight of the 2,6-di-tert-butyl-4-methylphenol represented in formula (9) (Junsei Co., Ltd.) were used as antioxidants, single layered electrophotographic photoreceptor of 20μm thickness was obtained by the same method as Example 1.

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### Example 4

Except that 0.5 parts by weight of the 2,6-di-tert-butyl-4-methylphenol represented in formula (9) were used as antioxidants, single layered electrophotographic photoreceptor of  $20\mu m$  thickness was obtained by the same method as Example 3.

### Example 5

Except that 5 parts by weight of the phenol compound represented in formula (14) (Ciba Specialty Chemical Co., Ltd., Irganox 1081) were used as antioxidants, single layered electrophotographic photoreceptor of  $20\mu m$  thickness was obtained by the same method as Example 1.

#### Example 6

Except that 5 parts by weight of the phenol compound represented in formula (10) (Ciba Specialty Chemical Co., Ltd., Irganox 259) were used as antioxidants, single layered electrophotographic photoreceptor of  $20\mu m$  thickness was obtained by the same method as Example 1.

### Example 7

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Except that 10 parts by weight of the phenol compound represented in formula (10) were used as antioxidants, single layered electrophotographic photoreceptor of 20µm thickness was obtained by the same method as Example 6.

### Example 8

Except that 5 parts by weight of the phenol compound represented in formula (11) (Ciba Specialty Chemical Co., Ltd., Irganox 3114) were used as antioxidants, single layered electrophotographic photoreceptor of  $20\mu m$  thickness was obtained by the same method as Example 1.

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### Example 9

Except that 5 parts by weight of the phenol compound represented in formula (12) (Ciba Specialty Chemical Co., Ltd., Irganox 1330) were used as antioxidants, single layered electrophotographic photoreceptor of  $20\mu m$  thickness was obtained by the same method as Example 1.

Comparative Example

Except that an antioxidant was not used, single layered electrophotographic photoreceptor of 20µm thickness was obtained by the same method as Example 1.

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The performance test on each electrophotographic photoreceptor prepared by examples 1-9 and comparative example were conducted as follows.

### **Electrostatic Characteristics**

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The electrostatic characteristics of each photoreceptor were evaluated by drum photoreceptor evaluation device (QEA Co., Ltd., "PDT-2000").

### Potential Maintenance Ratio (Dark Decay)

After charging the photoreceptors in +7.5 kV corona voltage, when a relative velocity between charger and the photoreceptor is 100mm/sec, a single color light of 780nm wavelength is irradiated in constant exposure energy within a range of 0- $10 mJ/m^2$ , and the surface potentials after the irradiation were measured. The potential maintenance ratio was determined by dividing surface potential before the irradiation,  $V_0$  with surface potential 1 minute after the irradiation,  $V_1$  (V) in dark pixel,

that is,  $V_1/V_0$ , and the results are shown Table 1.

Table 1

Sample	Type of antioxidant	Content of Antioxidant (parts by wt)	Vo	V <sub>1</sub> (V)	V₁N₀ (%)
Example 1	Formula 13	5	550	500	90.1
Example 2	Formula 13	10	528	484	91.6
Example 3	Formula 9	5	555	504	90.8
Example 4	Formula 9	0.5	500	470	94.0
Example 5	Formula 14	5	-1)	-	-
Example 6	Formula 10	5	538	470	87.4
Example 7	Formula 10	10	-1)	-	-
Example 8	Formula 11	5	570	505	88.6
Example 9	Formula 12	5	570	515	90.4
Comparative Example	-	-	500	420	84.0

1): not measured

### **Electrical Lifetime**

After charging the photoreceptors in +7.5 kV corona voltage, when a relative velocity between charger and the photoreceptor is 100 mm/sec, a single color light of 780 nm wavelength is irradiated in constant exposure energy within a range of  $0-10 mJ/m^2$ , and the initial surface potentials  $V_0$  (V) after the irradiation were measured.

Then, in the same condition as initial condition, antistatic processes with light exposure (about  $100\text{mJ/m}^2$  energy) by light emitting diode of 600nm wavelength were repeated  $1,000,\,5,000,\,8,000$  times 1 minute after charging. After the antistatic process, a single color light of 780nm wavelength is irradiated in constant exposure energy within a range of  $10\text{mJ/m}^2$ , and the surface potentials  $V_{1k}$  (V),  $V_{5k}$  (V), and  $V_{8k}$  (V), were measured to evaluate the electrical lifetime of the photoreceptor. The results are shown in Table 2.

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Table 2

Sample	V <sub>0</sub> (V)	V <sub>1k</sub> (V)	V <sub>5k</sub> (V)	V <sub>8k</sub> (V)	V <sub>8k</sub> /V <sub>0</sub> (%)
Example 1	710	680	580	550	77.5
Example 2	710	705	615	550	77.5
Example 3	810	804	790	780	96.3
Example 4	-1)	-	-	-	-
Example 5	900	870	840	780	86.7
Example 6	860	810	700	660	76.7
Example 7	910	900	800	-	-
Example 8	-1)	-	-	-	-
Example 9	-1)	-	-	-	-
Comparative	791	760	620	450	56.9
Example					

1) : not measured

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Referring to Table 1 and 2, the electrophotorgraphic photoreceptor according to the present invention has reduced dark decay, and maintains initial charging potential highly after repeated antistatic processes compared to the comparative example. Therefore, by using the electrophotorgraphic photoreceptor according to the present invention, it is possible to obtain good images even after the repeated uses. Consequently, the electrical lifetime of the photoreceptor is extended. It is probably because the antioxidants according to the present invention have the specific structures to prevent oxidizers such as ozone and nitric oxide (NOx) from oxidizing the photoreceptor including the binding resins, the electron transporting materials, and the hole transporting materials.

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### **Endurance Test**

To test the endurance of the photoreceptors according to example 1-9 against aliphatic carbohydrate solvent, which is conventionally used as liquid developer, solvent immersion test was performed as follows.

Solvent immersion test was carried out by dipping the sample photoreceptor in a container (500ml volume) filled with aliphatic carbohydrate solvent (Exxon Chemical Co. Ltd., 'Isopar L'), placing the container at room temperature (25  $^{\circ}$ C) for 5 days, and observing the status of the photoreceptor layer and solvent. The results are shown in Table 3.

Table 3

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	Solvent	Photoreceptor layer	
Example 1	No change	No change	
Example 2	No change	No change	
Example 3	No change	No change	
Example 4	No change	No change	
Example 5	No change	No change	
Example 6	No change	No change	
Example 7	No change	No change	
Example 8	No change	No change	
Example 9	No change	No change	

Referring to Table 3, the electrophotorgraphic photoreceptors according to example 1-9 of the present invention are not eroded by the immersion in the solvent. Therefore, even if these photoreceptors are used in wet developing method, in which the liquid developer directly contacts the surface of the photoreceptors, the photoreceptors are not eroded, and the developer is not contaminated, consequently, stabilized developing can be maintained. It is probably because that the photoreceptor according to the present invention uses the polyester resins of specific structure having biphenylfluorene unit represented in formula 1 or 3 in the main chain as a binder.

From the above description, it is evident that the electrophotographic photoreceptor according to the present invention is highly resistant to liquid developer by using

polyester resins with a specific structure as binding resins, produces good images even though it has single photoreceptor layer since a decrease in electrical potential of photoreceptor due to corona discharge is suppressed by using antioxidants with a specific structure, and has extended electrical lifetime. Therefore, it is possible to manufacture more practical electrophotographic devices with the aid of the electrophotographic photoreceptor according to the present invention.

### What is claimed is:

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1. An electrophotographic photoreceptor comprising:

a conductive substrate; and

a photoreceptor layer formed on said substrate comprising polyester resins which have biphenyl fluorene units of following general formula (1) in the main chain as binding resins, and phenolic compounds which have following general formula (2) as antioxidants:

Formula (1)

10 Formula (2)

$$X_{1} = X_{2}$$

$$X_{1} = X_{2}$$

$$X_{2}$$

wherein, in the formula (1), the hydrogens in the aromatic rings may or may not be substituted with substituents selected from a group consisting of halogen,  $C_1$ - $C_{20}$  aliphatic hydrocarbon, and  $C_5$ - $C_8$  cycloalkyl;

wherein, in the formula (2),  $X_1$  and  $X_2$ , independently each other, are hydrogen or  $C_1$ - $C_6$  alkyl,  $Y_1$  and  $Y_2$ , independently each other, are hydrogen, methyl or ethyl, and  $X_3$  is selected from a group consisting of following  $C_1$ - $C_6$  alkyls;

$$\frac{Y_1}{\text{CH}_2} \frac{X_1}{\text{COO}_b} \text{CH}_2 \frac{Y_1}{\text{C}} = \frac{X_1}{\text{II}} \text{OH}$$

$$Y_2 = \frac{X_1}{\text{II}} \text{OH}$$

or 
$$\begin{array}{c|c} X_1 & X_1 & X_1 \\ X_1 & X_2 & X_3 & X_4 & Y_2 \end{array}$$

wherein, in  $X_3$ , a, c, k, I, and m is an integer of 0 to 6, b is 0 or 1,  $X_1$  and  $X_2$ , independently each other, are hydrogen or  $C_1$ - $C_6$  alkyl,  $Y_1$  and  $Y_2$ , independently each other, are hydrogen, methyl or ethyl, and  $X_4$ ,  $X_5$ , and  $X_6$ , independently each other, are hydrogen or  $C_1$ - $C_6$  alkyl.

2. An electrophotographic photoreceptor comprising: a conductive substrate; and

a photoreceptor layer formed on said substrate comprising polyester resins which have biphenyl fluorene units of following general formula (1) in the main chain as binding resins, and phenolic compounds which have following general formula (3) as antioxidants:

Formula (1)

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Formula (3)

$$\begin{bmatrix} X_1 & & & \\ X_1 & & & \\ &$$

wherein, in the formula (1), the hydrogens in the aromatic rings may or may not be substituted with substituents selected from a group consisting of halogen,  $C_{1}$ - $C_{20}$  aliphatic hydrocarbon, and  $C_{5}$ - $C_{8}$  cycloalkyl;

wherein, in the formula (3),  $X_1$  and  $X_2$ , independently each other, are hydrogen or  $C_1$ - $C_6$  alkyl, a and c is an integer of 0 to 6, b is an integer of 0 or 1, n is an integer of 2 to 4, Z is S or O when n is 2, N when n is 3, and C when n is 3.

3. The electrophotographic photoreceptor according to claim 1 or 2, said polyester resin may be a polyester resin comprising repeating units of following

general formula (4), (5) or (6), or a copolymer comprising more than two of the repeating units.

## Formula (4)

## 5 Formula (5)

# Formula (6)

$$-0$$

4. The electrophotographic photoreceptor according to claim 1 or 2, said polyester resin may be a compound of a following general formula (7) or (8). Formula (7)

Wherein, m and n, independently each other, are an integer of 10 to 1,000. Formula (8)

Wherein, k is an integer of 10 to 1,000.

- 5. The electrophotographic photoreceptor according to claim 1 or 2, the content of said antioxidant may be from 0.01wt% to 50wt% of the total weight of said charge transporting material of said photoreceptor layer.
- 6. The electrophotographic photoreceptor according to claim 1, said antioxidant of the general formula (1) is a compound selected from a group consisting of compounds of general formula (9), (10), (11) and (12).

Formula (9)

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# Formula (10)

# Formula (11)

# 5 Formula (12)

7. The electrophotographic photoreceptor according to claim 2, said antioxidant of the general formula (3) is a compound of general formula (13) or (14).

Formula (13)

Formula (14)

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- 8. The electrophotographic photoreceptor according to claim 1 or 2, said electrophotographic photoreceptor is a electrophotographic photoreceptor for a wet developing method.
- 9. An electrophotographic device with the electrophotographic photoreceptor according to anyone of claims 1 to 8.

### Abstract of the Disclosure

A single layered electrophotographic photoreceptor with a photoreceptor layer comprising polyester resins which have biphenyl fluorene units in the main chain as binding resins, and specific phenolic compounds as antioxidants is disclosed. The electrophotographic photoreceptor according to the present invention makes it possible to obtain better image by suppressing a decrease in dark decay and electric potential due to repeated use, and its electrical lifetime is extended.